DNA Bases as Molecular Electronic Devices

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ABSTRACT
The current voltage characteristics have been obtained for the four DNA bases Adenine, Thymine, Guanine and Cytosine by non-equilibrium Green's function combined with density functional theory. The pattern of current flow for an applied voltage sweep of 0-5 V is plotted. The phenomenon of tunneling is exhibited in the characteristics of molecules. The DNA base cytosine displays a typical surge of current in the voltage sweep section of 0.4V-0.6V, indicating single electron effects. The effect of gate voltage on the current-voltage characteristics of cytosine was studied in the gated two-probe setup. The typical section of characteristics of cytosine was re-drawn by varying the gate potential. The application of gate bias exhibits excellent ON/OFF switching for combinations of the two applied voltages- source voltage and gate voltage. Repetitive peaks are also observed in current when gate voltage is varied, fixing source potential. In this paper the cytosine molecule is proposed as a switch, AND gate and OR gate in this paper that can be used in DNA based molecular electronic devices.

Keywords: DNA bases, tunneling, single electron effects, molecular electronic devices.

1. INTRODUCTION
The zest for high speed electronic systems supported by dense memories is pushing integrated circuits into the realm of nanoelectronics. For a nanoelectronic device, the element can be a carbon nanotube or a semiconducting nanowire. Molecules also provide an interesting option for use as an element in nanoelectronic devices. Molecular electronics tends to utilize the electronic properties of certain molecules as nature has been doing for millions of years. Since the molecules are very small, their functionality can be tuned. Development of molecular and nanoelectronic components such as wires, diodes, transistors, oscillators and switches [1,2] as well as the conceptual discussion of their current-voltage properties have greatly enhanced the zeal for designing novel molecular systems with typical electronic properties. Several attempts have been made to theoretically explain the current-voltage characteristics of the molecular systems [3, 4] There are various candidates for molecular devices such as-organic polymers [5, 6] large bio-molecules [7, 8], nanotubes & fullerenes [9, 10]. DNA the carrier of genetic information is one of the promising candidates for molecular electronics. Self-replication property of DNA renders it as most suitable for creation of identical molecular electronic devices. A DNA chain consists of a long polymer composed of four subunits (nucleotide) containing the bases adenine (A), thymine (T), guanine (G) and cytosine (C) attached to the repetitive sugar-phosphate backbone almost like beads strung on a necklace. The bases form an interesting subject for use in single molecule electronics. In this paper the current-voltage characteristics have been obtained for the four DNA bases A, T, G and C and they have been analysed for use in molecular electronic devices.

2. COMPUTATIONAL METHOD
The molecular structures of the DNA base molecules were created using HYPERCEM 7 software. The four bases A, T, G and C were obtained with backbone attached to them. The backbone was removed from the single strand structures and the open bond was terminated using a hydrogen atom. Virtual Nanolab software was used to perform calculations, which is an *ab initio* electronic structure program capable of simulating and modeling electrical properties of nanostructured systems coupled to semi-infinite electrodes. Non-equilibrium Green's functions (NEGF) and density functional theory (DFT) are combined in the software and the entire system was treated self-consistently under finite bias conditions [11].We used LDA-PZ, which is the local density approximation (LDA) with the Perdew-Zunger (PZ) parametrization [12] of the correlation energy of a homogeneous electron gas calculated by Ceperly-Alder [13]. In these *ab initio* electronic structure computations, we used the Double Zeta Polarization (DZP) basis set. Gold was used to construct thin electrodes as it is a practical choice and a promising monoatomic nanowire [14]. The current is calculated using Landauer's formula which expresses the conductance of a system at T=0 in terms of the quantum mechanical transmission coefficients [15].

$$I = \int_{\mu_L}^{\mu_R} T\,(E, V_S)\,dE$$

where μ_L and μ_R are the left- and right-side metallic reservoirs electrochemical potentials and T (E, V_S) is the transmission probability for electrons incident at an energy E through a device under a potential bias V_S. The Landauer equation based on the Green's function method relates the elastic conductance of a junction to the probability that an electron with energy E injected in one electrode will be transmitted to another electrode through a scattering region which in our case are the DNA bases. Using the above-mentioned procedure we calculated current-voltage (I-V) characteristics of the four DNA bases A, T, G and C. The effect of gate potential on the characteristics of DNA base Cytosine was also studied by enabling the gate and providing gate bias.

3. CURRENT FLOW THROUGH DNA BASES

To study the current voltage characteristics the DNA bases are placed between two gold electrodes one as source and other as drain. The positive voltage V_S is applied at source fixing the drain potential V_D at 0V. This potential difference will maintain them at distinct potentials so that;

$$\mu_L - \mu_R = qV_S$$

thus giving rise to two different Fermi functions which are expressed as:

$$f_L(E) = f_0(E - \mu_L) = \left\{1 + \exp\left[\frac{E - \mu_L}{K_B T}\right]\right\}^{-1}$$

$$f_R(E) = f_0(E - \mu_R) = \left\{1 + \exp\left[\frac{E - \mu_R}{K_B T}\right]\right\}^{-1}$$

Each contact seeks to bring the channel into equilibrium with itself. The quest to achieve equilibrium causes the current to flow from source to drain.[16]

The molecular structure of DNA bases created in HYPERCHEM 7 were inserted between two gold terminals using the two probe setup of Virtual Nanolab software forming metal-molecule-metal assembly as shown in Fig 1. The molecules are chemisorbed onto the electrodes, and the above orientation is fixed, although these molecules being asymmetric, the current-voltage characteristics will be varying greatly with orientation. A voltage bias V_S varying from 0-5V was applied to the four respective bases and the corresponding current values were obtained.

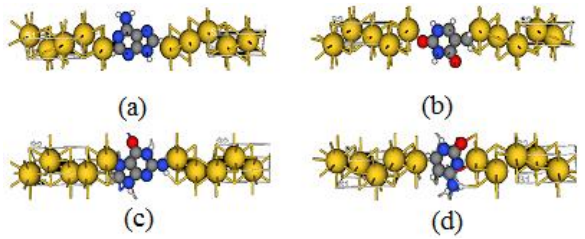

Fig 1. DNA Bases inserted between gold terminals (a) Adenine (b) Guanine (c) Thymine (d Cytosine. Yellow balls are presenting Gold, Blue as nitrogen, Grey as Carbon and red as Oxygen in electrode-molecule-electrode assembly.

The current voltage characteristics for the four DNA bases are shown in Fig 2 (a) and (b). The curves illustrate flow of tunneling current through the molecules. The current voltage characteristics of single ringed DNA bases Adenine and Guanine (pyramidines) display smooth tunneling process as shown in Fig 2(a) where the magnitude of current is in the range of nanoamperes.The curves are also marked by resonant tunneling peaks. For Adenine molecule, peak current of 0.22 nA is observed for an applied source bias of 1.5 V; while peak current of 0.87nA is observed in Guanine molecule for an applied bias of 1.4 V.

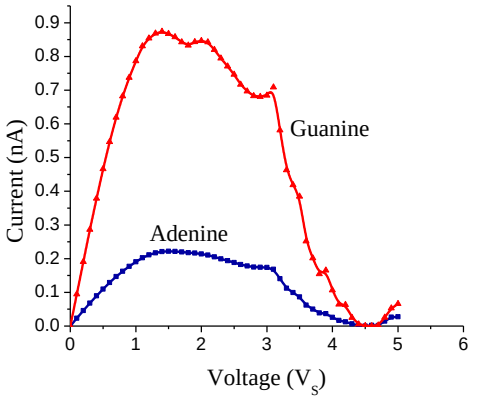

Fig. 2 (a) Current-voltage plot for Adenine & Guanine

The double ringed DNA bases (purines) display a very interesting pattern of current flow which is shown in Fig 2(b). The DNA base Cytosine shows a sudden surge of current in its characteristics. The value of peak current is 6.39 µA for an applied bias of 0.6 V. The characteristics of Thymine display an oscillating behavior where the current shuffles between peaks and valleys. The magnitude of the current is in microamperes. Though the magnitudes of current are very small, the current densities are going to be very large virtue the small size of molecules. These densities will be able to drive the electronic circuits.

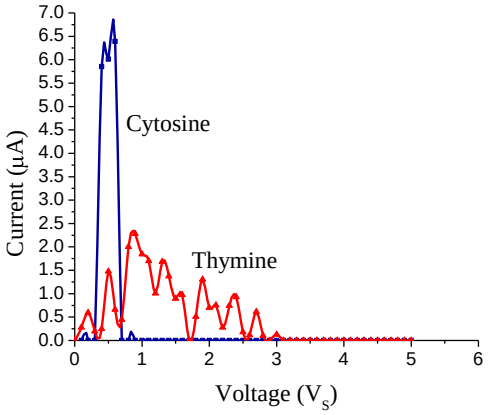

Fig. 2 (b) Current-voltage plot for Cytosine & Thymine

4. EFFECT OF GATE POTENTIAL ON DNA BASE CYTOSINE

The current voltage characteristics of the DNA base Cytosine display a very interesting pattern. When the voltage sweep of 0-5 V is applied at the source on gold-cytosine-gold assembly, a sudden surge of current is observed for applied source voltage of value 0.4-0.6 V. The typical pattern inspired the detailed probing of the characteristics of the molecule. To do so a third terminal gate was added to the two probe structure that is schematically represented in Fig.3. and is called Cytosine based Molecular Transistor.

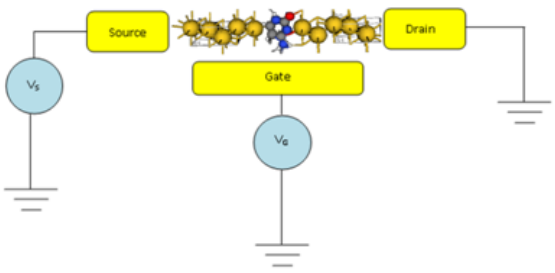

Fig 3. Schematic representation of gated Gold-Cytosine-Gold structure

The current flowing between source and drain for a voltage sweep of -0.4V to 0.4 V was calculated while varying gate potential from -0.4V to 0.4V in incremental steps of 0.1V. From the values obtained, a set of current-voltage characteristics was plotted for Current I flowing between source and drain wrt voltage applied at source V_S; keeping gate potential V_G constant. Another set of current-voltage curves was plotted between current I and gate potential V_G maintaining constant source potential V_S. The analysis has been done on selective data that displayed typical values.

4.1 Current versus Source Voltage (V_S) at Constant Gate Voltage (V_G)

The set of characteristics between the source potential and the corresponding current were obtained for various gate potentials. Nine sets of current voltage values were obtained for gate potentials varying from -0.4V to +0.4V in steps of 0.1V. It is observed from the curves plotted that for V_G = 0V, the current suddenly rises from 4.84X 10^{-2} nA to 5.85 µA for change of source voltage from 0.3V to 0.4V displaying On/Off kind of behavior.

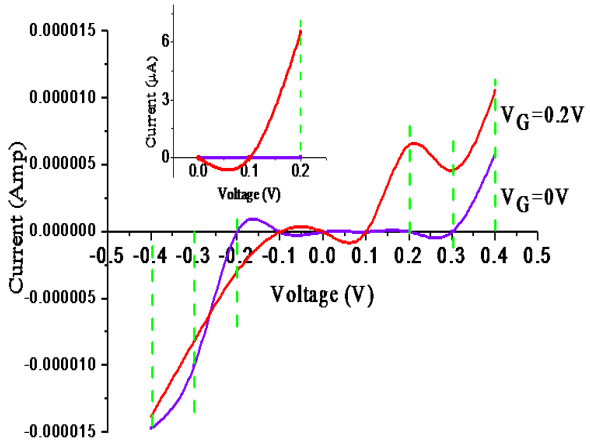

Fig 4. Current v/s Voltage (V) for constt V_G

The typical behavior of sudden increase in conductivity of the molecule can be similarised to single electron effect. When the gate potential is applied, the energy levels of the molecule are shifted higher in case of negative gate potential and are lowered in case positive potential; thus altering the conductivity pattern. The current-voltage curve plotted for a source voltage sweep of -0.4 V to 0.4V with gate voltage V_G fixed at 0.2V is characteristically interesting as seen in Fig.4. It is seen that current changes from 1.62X 10^{-2} nA to 6.5 µA when V_S is increased from 0.1V to 0.2V and current stays in µA range for higher voltages of the sweep. This implies that the current goes high if the gate voltage V_G is varied from 0V to 0.2V fixing source at 0.2V.

4.2 Current versus Gate voltage (V_G) at Constant Source Voltage (V_S).

Another set of current-voltage characteristics was plotted between current and gate voltage for constant source voltage. The source voltage was varied from -0.4 to 0.4V in steps of 0.1V. Fixing the source at various source voltages, the current was obtained by sweeping gate voltage V_S from -0.4V to 0.4V. It is observed that the current flow through the assembly displays repetitive peak values when the gate voltage sweep is applied fixing the source potential at 0.2V and 0.3V. The pattern of current variation as shown in Fig. 5 can be related to the coulombic oscillations. This is due to resonant tunneling via molecular orbitals of cytosine that provide an open path for conduction whenever aligned with the Fermi level. For small source voltages of value ± 0.1V there is a constant flow of very small current of the 1.6X10^{-2} nA .

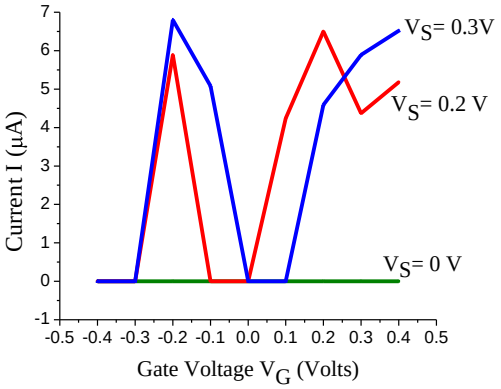

Fig 5. Current v/s Gate Voltage (V_G) for constt V_S

The study of conductivity in cytosine molecule has created a very interesting pattern. The conductivity of the molecule is very high if we apply a gate potential of 0.2V and apply a source potential of 0.2 V or -0.2V, though the current flowing in the two cases is opposite in direction. Similar type of transition in conductivity is observed for fixed source voltage of 0.2V and gate potential varying from 0 to 0.2 V or 0 to -0.2V. The suppression of current around zero source voltage with zero gate potential is called coulomb blockade characteristics.

5. MOLECULAR GATES

Logic gates are the backbone of digital electronics. They are building blocks of combinational and sequential circuits which can be used as counters, registers and memories. The logic gates can be designed using switches, relays, transistors etc.The switching behavior of the cytosine molecule can be used to design logic gates. In this paper we propose design for a switch which can be used in AND and OR gate using Cytosine based molecule transistor.

5.1 Cytosine based Molecular Switch

The current-voltage data obtained for the cytosine molecule as shown in Table 1 exhibited excellent switching pattern.

Table 1. Current flowing through gold-cytosine-gold assembly corresponding to various source and gate voltages.

Voltage (V)	V_G =-0.2	V_G =0	V_G =0.2
V_S = -0.2	-3.239e-11A (OFF)	-3.239e-011A (OFF)	-2.98e-006A (ON)
V_S = 0	0.0 (OFF)	0.0 (OFF)	0.0 (OFF)
V_S = 0.2	5.892e-006A (ON)	3.237e-011A (OFF)	6.501e-006A (ON)

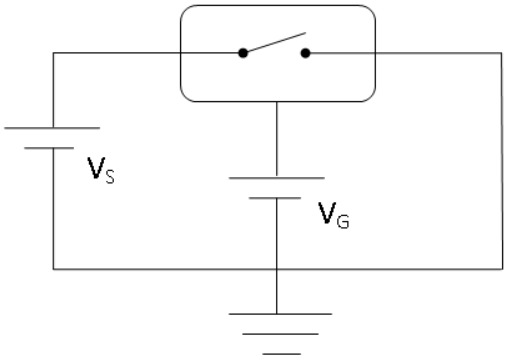

Fig 6. Schematic of a switch

It is observed that the switch will be always OFF (open) for V_G = 0V for all values V_S. Similarly it also remains OFF (open) for V_S = 0V for all values of V_G. A current in the range of 10^{-2} nA flows through the device if a voltage of 0.1V is applied to any of the terminals which is very small, hence can be approximated as zero and considered as logic LOW. The switch goes ON (closed) for voltage combinations as indicated in the Table. , where the current is in µA range and can be considered as logic HIGH. So the switch can be operated in two ways; i) Fixing gate potential V_G at 0.2V and varying V_S in the Table, ii) Fixing the source potential V_S at 0.2 V and varying value of V_G as indicated in the Table 1.

5.2 Cytosine based AND Gate

The AND gate is the "all or nothing gate" which can be expressed as a cascade of two switches as shown in Fig.7. The AND gate is a three terminal device with two inputs A and B and a single output labeled as Y. A and B inputs correspond to the source and gate terminal whereas output terminal Y is drain terminal. As the two switches are in series with the LED, it will light up when both the switches are closed. This means that for the LED to glow appropriate bias (0.2V) must be applied to the two switches through the battery. Further the gate bias of both the switches should be high (0.2V), so that right combination of two potentials take the cytosine based transistor into ON state and the LED glows which indicates completion of the circuit loop. The AND operator is denoted by a dot and the symbol of gate is as shown in the Figure 7.

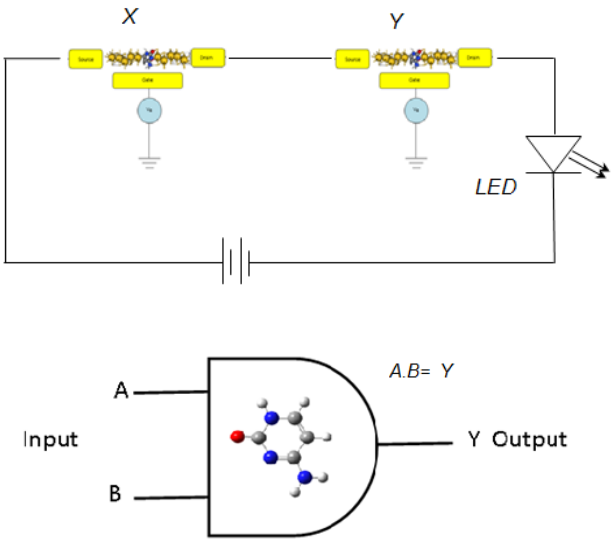

Fig 7. Cytosine based AND Gate

5.3 Cytosine based OR Gate

The OR gate is also known as the "any or all gate". Fig.8 illustrates the basic concept of an OR gate using switches. As clear from the figure there are two paths for the current to complete the circuit. So the LED will low when either or both the switches are ON. As the voltage for source bias is same for both of the switches, the gate potentials will decide the status of switches, hence the glowing of LED. The OR operator is denoted by '+' sign between the two input variables and the symbol of OR gate is shown in Fig 8.

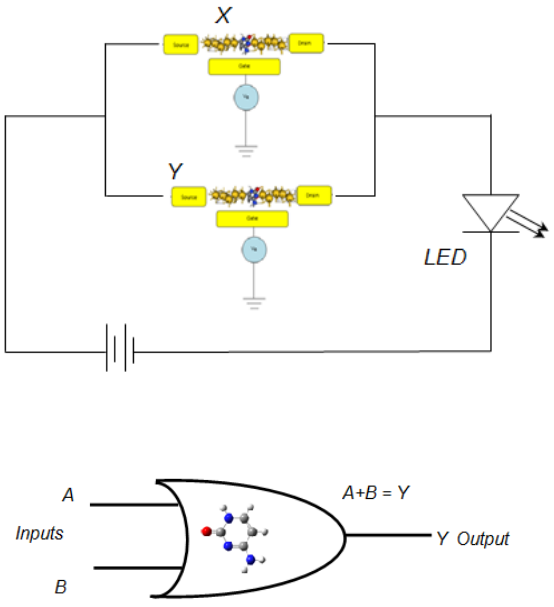

Fig 8. Cytosine based OR Gate

6. CONCLUSION

The current- voltage characteristics have been plotted for the four DNA bases A, T, G and C in this paper using Virtual Nanolab. The comprehensive study of the characteristics displays flow of tunneling current through the four bases. The current flowing through purine DNA bases G and A is of nA range and is of µA range for pyrimidine DNA bases C & T. The typical surge of current in the i-v plot for cytosine implying single electron characteristics motivated detailed probing of the characteristics of the molecule by adding the third terminal 'gate' to the two probe structure of the gold-cytosine-gold assembly. The increase in value of current on application of gate potential confirmed the single electron effects in the molecule. Hence the three terminal assembly can be considered as a transistor. The suppression of current around zero source voltage with zero gate potential is called coulomb blockade. The detailed probing of gated current-voltage characteristics has shown that switching behavior which can be exploited to use the cytosine based transistor as a molecular switch. This switch is used to assemble the circuits acting as AND gate and OR gate. The cytosine based transistor can be used as a memory as you can control the ON/OFF pattern by applying adequate bias. Organic LED's can be used in the circuits to further improve the molecular circuits.

7. REFERENCES

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